some water <1

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C09K 5/00

A1

(11) International Publication Number: WO 89/09806

(43) International Publication Date: 19 October 1989 (19.10.89)

(21) International Application Number: PCT/US89/01544

(22) International Filing Date: 13 April 1989 (13.04.89)

(30) Priority data:
181,788 15 April 1988 (15.04.88) US

(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventors: RENY, Gregory, P. ; 1008 Frost Avenue, Sarnia, Ontario N75 4G8 (CA). HAYMAN, Oliver, B. ; 41142 Village Lake Road, Novi, MI 48050 (US).

(74) Agent: FIFIELD, David, H.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU.

Published
With international search report.

(54) Title: INHIBITED ALKYLENE GLYCOL COOLANT AND COOLING PROCESS

(57) Abstract

A coolant composition containing (1) an alkylene glycol such as propylene glycol, (2) a corrosion inhibitor combination of an azole such as tolyltriazole, a molybdate salt and phosphoric acid and (3) less than 10 weight percent of water exhibits high temperature stability and corrosion inhibition for metals used in internal combustion engine cooling systems, particularly such metals as aluminum and magnesium and a process of cooling such an engine.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BG	Bulgaria
BJ	Benin
BR	Brazil
CF	Central African Republic
CG	Congo
CH	Switzerland
CM	Cameroon
DE	Germany, Federal Republic of
DK	Denmark
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
HU	Hungary
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
RO	Romania
SD	Sudan
SE	Sweden
SN	Senegal
SU	Soviet Union
TD	Chad
TG	Togo
US	United States of America

INHIBITED ALKYLENE GLYCOL COOLANT AND COOLING PROCESS

This invention relates to corrosion inhibited alkylene glycol compositions useful as coolants for the heat-exchange system of an internal combustion engine and to the process of using same to cool such an engine.

Presently, antifreeze compositions containing alcohols, especially ethylene glycol, are commonly mixed with equal or larger volumes of water in the cooling systems of internal combustion engines in order to depress the freezing point of the water. Such alcohols, in combination with the water in the cooling systems, produces acidic products which contribute to the corrosion of metal surfaces that contact the cooling system. Thus the uninhibited antifreeze compositions promote corrosion of brass, copper, solder, steel, cast iron and in more recent engines, aluminum and magnesium.

In the past a large number of corrosion inhibitors and combinations thereof have been employed in such aqueous-base antifreeze compositions. Such

inhibitors have included the alkali metal chromates, nitrates, phosphates, borates, tungstates, molybdates, carbonates and silicates and alkaline earth metal borates. Inhibitors have also included organic compounds such as carboxylic acids, thiocyanates, phenols, mercaptans, mercaptothiazoles and various aromatic triazoles. Many of such inhibitors, such as the silicates, deplete quickly and are no longer available for continued metal protection. Others, such as nitrites, which function well as inhibitors against the corrosion of iron or steel actually promote the corrosion of aluminum or magnesium.

Recently in an attempt to develop an improved cooling system from the standpoint of fuel efficiency and cooling efficiency, a cooling process was developed which employed a coolant containing little or no water. U.S. Patents 4,550,694 and 4,630,572. The primary means by which this system achieves the improvement in engine efficiency is to run the engine at higher than normal engine temperatures. Such higher temperatures often degrade many of the corrosion inhibitors such as the silicates at an even faster rate. Also, it has been found that uninhibited glycols used as anhydrous coolants are corrosive to typical cooling system components.

Therefore it is highly desirable to provide an inhibited coolant composition which is capable of functioning at temperatures in excess of 105°C, but which will not corrode the metal which is commonly used in the cooling systems of internal combustion engines.

The present invention is such a composition which comprises (1) at least 90 weight percent of an alkylene glycol or a mixture of two or more alkylene glycols and (2) a corrosion-inhibiting amount of an inhibitor comprising (a) from 0.02 to 4 weight parts of an azole, (b) from 0.05 to 3 weight parts of a molybdate salt and (c) from 0 to 3 weight parts of phosphoric acid. It also is a process of cooling an internal combustion engine by circulating said composition, as coolant, through the cooling jacket of said engine.

By employing (1) alkylene glycol as at least 90 weight percent of the coolant and (2) the aforementioned combination of corrosion inhibitors, metals such as aluminum and magnesium can be used in components, e.g., radiator, coolant pump, engine block, cylinder head, of the cooling system. The coolant composition can be employed in engines operating at temperatures higher than normal without degrading. As a result the engines are more fuel efficient and produce combustion products that are less offensive to the environment than those operating at conventional temperatures of less than 100°C.

While the coolant compositions of this invention are particularly suitable for use in a process for cooling in internal combustion engines, they are also usefully employed in other applications such as heat-transfer fluids or hydraulic fluids.

Alkylene glycols suitably employed as the coolant in the compositions of this invention are those dihydric alcohols which are liquid at temperatures in

the range of -65°C to -30°C and which boil at atmospheric pressure at temperatures in the range from 150°C to 230°C. Examples of such glycols include ethylene glycol, propylene glycol, glycerol and mixtures of two or more thereof in any proportion. Preferred glycols are ethylene glycol, propylene glycol and mixtures thereof. More preferably, the alkylene glycol is propylene glycol or a mixture of at least 30 weight percent of propylene glycol and from 0.1 to 70 weight percent of ethylene glycol. Use of propylene glycol is most preferred.

The corrosion inhibitor combination employed in the coolant composition suitably comprises and preferably consists essentially of (a) from 0.06 to 0.5 weight parts of the azole, (b) from 0.1 to 0.2 weight parts of the molybdate salt and (c) from 0.05 to 0.09 weight parts of phosphoric acid.

A suitable corrosion - inhibiting amount of the inhibitor combination may be determined empirically by use of standard corrosion tests with samples of varied quantities of the inhibitor combination. Since some users may ascribe greater importance to one test than another, the significance of corrosion testing is relative and not absolute. However, the ASTM test methods described in the working examples are commonly employed.

Typically, in the total coolant composition, from 0.05 to 2 weight percent of the inhibitor combination is suitable and preferably from 0.1, more preferably 0.25 up to 1, more preferably 0.75 weight percent of the inhibitor combination is employed.

The azole which is used in the practice of this invention is any azole which is soluble in the alkylene glycol and which is a corrosion inhibitor for copper and brass. The azole is preferably a triazole such as tolyltriazole, benzotriazole and mixtures of two or more thereof. Tolyltriazole is most preferred. Other azoles which are suitable but less preferred than the aforementioned triazoles include thiazoles such as mercaptobenzothiazole, and alkali metal salts of such azoles.

Molybdate salts employed in the inhibitor combination are those which are soluble in the alkylene glycol and which are corrosion inhibitors for steel and cast iron. Such salts include the molybdates of the alkali metals and alkaline earth metals. Examples of preferred molybdates are sodium molybdate, ammonium molybdate, potassium molybdate and mixtures of two or more thereof. Sodium molybdate is most preferred.

The phosphoric acid is employed to maintain the pH of the coolant composition in the range from 7 to 9, preferably from 7 to 8, and only if necessary. Some alkylene glycol mixtures are within the pH limits, and in such cases no pH adjustment is required.

The coolant composition of this invention is prepared by first dissolving up to 10 weight percent of water in the alkylene glycol. Preferably less than about 5 weight percent and more preferably about 3 percent of water is dissolved in propylene glycol. Most preferably the alkylene glycol is used with essentially no water, i.e., less than about 1 weight percent. Subsequently, the corrosion inhibitor

combination is dissolved into the alkylene glycol composition. Preferably, the resulting coolant composition is then rendered basic by adding sodium or potassium hydroxide until a pH of from 7 to 9 is reached, or phosphoric acid is added if the initial pH value of the alkylene glycol base fluid is too alkaline. Optionally other ingredients such as dyes and antifoaming agents, e.g., those disclosed in U.S. Patents 3,340,309; 3,504,041; 3,770,701 and 2,425,755, can be added to the composition. While anti-foam additives are not required, they may nevertheless be employed.

The process of cooling an internal combustion engine is carried out by circulating the coolant composition of the invention through the cooling jacket of the engine. The invention composition is designed to be used "as is", i.e. a full fill coolant, in cooling equipment such as described in U.S. Patent 4,550,690 previously mentioned, at ambient pressures, e.g. atmospheric pressure, yet to avoid corrosive effects on the metal components of such cooling equipment by use of the carefully chosen corrosion inhibitor combination.

The cooling process is preferably carried out at a coolant operating temperature range of 105°C to 150°C, temperatures previously noted above. More preferably the operating temperature range of the coolant is above 110°C, most preferably above 120°C and more preferably below 140°C, most preferably below 135°C.

Preferably the coolant composition contains not more than 5 weight percent, more preferably not more

than 3 weight percent and most preferably not more than 1 weight percent water.

The preferred composition of the corrosion inhibitor package is the same as previously noted above and most preferably consists essentially of an azole, a molybdate salt and optionally the phosphoric acid when pH adjustment is desired. The amounts of each component to be employed are also noted previously in the text.

The following examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

Examples 1-2

A coolant concentrate is prepared by dissolving about 1 part of tolyltriazole, about 0.6 part of sodium molybdate dihydrate and about 0.3 part of an 85 percent solution of phosphoric acid in water, in 20 parts of propylene glycol containing 4 parts of water. The resulting concentrate is then combined with 370 parts of propylene glycol to form the coolant composition which has a pH (100-ml sample diluted 1:1 in water) in the range from 6 to 7. The anhydrous coolant composition is then tested for corrosion inhibition. The resulting coolant's composition is described in and the test results are reported in Table I.

An additional coolant composition (Example No. 2) is similarly prepared using a mixture of ethylene glycol and propylene glycol as the alkylene glycol blend. This composition is similarly tested for cor-

rosion inhibition. The coolant's composition and the results of these tests are also reported in Table I.

For purposes of comparison, a control coolant composition is prepared using propylene glycol (Example No. C_1) and 30/70 mixture of uninhibited propylene glycol and ethylene glycol (Example No. C_2). These compositions are also tested and the results of those tests are also reported in Table I.

TABLE I

Example No.	1	2	C_1*	C_2*
Glycol®, wt pts				
PG	100	30	100	30
EG	0	70	0	70
Water, wt pts	1	1	<1	<1
Azole®, wt pts				
TT	0.25	0.25	0	0
Molybdate, wt pts $Na_2MoO_4 \cdot 2H_2O$	0.15	0.15	0	0
H_3PO_4 (85%)	0.075	0.075	0	0

TABLE I (oont'd)

Example No.	1	2	C_1*
Corrosion Inhibition,			
wt loss in 336 hours			
Glassware® Corrosion, mg wt loss**			
Cu	13.7	1.9	8.8
Solder	9.0	41.8	93.2
Brass	0.6	1.1	104.3
Steel	0.5	+6.5	239.8
Mg	1.3	1015.5	>2000.0
Al	0.3	+11.1	+0.7
wt loss in 336 hours			
Glassware® Corrosion, mg wt loss**			
Cu	0.5	1.9	36.5
Solder	6.6	31.2	868.3
Brass	0.0	0.7	17.8
Steel	+0.1	0.0	21.8
Cast Iron	+0.2	+0.4	5.0
Al	0.3	+0.2	+6.8

TABLE I (cont'd)

Example No.	1	2	C_1*	C_2*
Corrosion Inhibition,				
Heat Rejecting Metal Surface Test⑤, weight loss, mg/cm²/week (168 hr)				
Al	0.085	-	0.67	0.21
Mg***	0.19	2.77	5.79	-
Engine Dynamometer Corrosion Test⑥, mg wt loss** after 672 hours				
Cu	24.0	-	-	-
Solder	8.6	-	-	-
Brass	1.3	-	-	-
Steel	0.6	-	-	-
Cast Iron	0.0	-	-	-
Al	0.6	-	-	-

* Not an example of the invention
** Weight loss in milligrams is measured using a standard coupon for the test having an area 5 cm by 2.5 cm (2 inches by one inch)
*** Same method as used for Al except Mg coupon is cleaned with 20% chromic acid in place of the 2% chromic acid - 5% orthophosphoric acid mixture of ASTM D-4340,
① PG - propylene glycol, EG - ethylene glycol
② TT - tolyltriazole
③ ASTM D-1384
④ ASTM D-4340 - modified to use neat fluid, without ASTM corrosive water.
⑤ Engine dynometer test using a Ford Escort 4-cylinder engine operating at a ΔT of 19.4°C (35°F) across the radiator and at a ΔT of 8.3°C (15°F) across the heater core and overall average engine operating temperature of 107°C (225°F).

As evidenced by the data set forth in Table I, the coolant compositions of this invention exhibit good corrosion inhibition for both aluminum and magnesium when the coolant compositions are exposed to temperatures in excess of 105°C for periods up to 672 hours.

CLAIMS :

1. A coolant composition comprising (1) at least 90 weight percent of an alkylene glycol or a mixture of two or more alkylene glycols and (2) a corrosion-inhibiting amount of an inhibitor comprising (a) from 0.02 to 4 weight parts of an azole, (b) from 0.05 to 3 weight parts of a molybdate salt and (c) from 0 to 3 weight parts of phosphoric acid.

2. The composition of Claim 1 wherein the alkylene glycol is propylene glycol or a mixture of at least 30 weight percent of propylene glycol and from 0.1 to 70 weight percent of ethylene glycol.

3. The composition of Claim 2 wherein the composition contains no more than 5 weight percent of water.

4. The composition of Claim 2 wherein the composition contains no more than 1 weight percent of water.

5. The composition of Claim 4 wherein the alkylene glycol consists solely of propylene glycol.

6. The composition of Claim 2 wherein the azole is a triazole.

7. The composition of Claim 6 wherein the triazole is tolyltriazole, benzotriazole and mixtures thereof.

8. The composition of Claim 2 or 4 wherein the azole is tolyltriazole.

9. The composition of Claim 6 wherein the azole is mercaptobenzothiazole.

10. The composition of Claim 2 wherein the molybdate salt is an alkali metal molybdate.

11. The composition of Claim 2 or 4 wherein the molybdate salt is sodium molybdate.

12. The composition of Claim 5 wherein are present (a) tolytriazole, (b) sodium molybdate and (c) phosphoric acid in the respective amounts of (a) 0.25, (b) 0.15, and (c) 0.075 percent by weight of the composition.

13. A process for removing heat generated in the operation of an internal combustion engine by circulating through the cooling jacket of said engine, a coolant which is exposed to approximately the ambient pressure of the surrounding environment at a coolant operating temperature above 105°C, having the improvement of employing as said coolant a liquid composition having low corrosivity toward the materials of construction with which said coolant is in contact,

which composition is the coolant composition defined by Claim 1.

14. The process of Claim 13 wherein the alkylene glycol consists essentially of propylene glycol or a mixture of at least 30 weight percent propylene glycol and from 0.1 to 70 weight percent ethylene glycol and the coolant composition contains no more than 5 weight percent water.

15. The process of Claim 14 wherein the coolant composition contains no more than 1 weight percent water and the alkylene glycol consists solely of propylene glycol.

16. The process of Claim 14 or 15 wherein
(a) the azole is tolyltriazole
(b) the molybdate is sodium molybdate.

17. The process of Claim 14 or 15 wherein
(a) the azole is tolyltriazole present in 0.25 weight percent,
(b) the molybdate is sodium molybdate present in 0.15 weight percent and
(c) phosphoric acid is present in 0.075 weight percent, of the composition weight.

18. The process of Claim 14 or 15 wherein the coolant operating temperature is normally in the range between 110° and 140°C.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/01544

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): C09K 5/00
U.S. CL. 252/75

II FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	252/74, 75, 77

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No [13]
Y	US, A, 4,440,721, (Wilson et al), 04 April 1984, (Note the entire document)	1-18
Y	US, A, 4,450,088, (Wilson et al), 22 May 1984, (Note column 3, lines 32-42)	2,5,14,15
Y	US, A, 4,382,870, (Abel et al), 10 May 1983, (Note column 2, lines 1-4)	2,5,14,15
Y	US, A, 4,550,694, (Evans et al), 05 November 1985, (Note Abstract)	13
Y	US, A, 4,630,572, (Evans et al), 23 December 1986, (Note Abstract)	13
Y	Derwent Abstracts, Accession Number 83-811019/45, "Corrosion Inhibitor for Aluminum in Engine Cooling System"; corresponds to Japanese Patent J58164792-A 29 September 1983, (Note Abstract)	1,6-8,10-12

* Special categories of cited documents: [10]
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
06 June 1989	17 JUL 1989
International Searching Authority	Signature of Authorized Officer
ISA/US	Christine A. Skane Christine A. Skane